

***Interactive comment on* “Comparison of secondary organic aerosol formation from toluene on initially wet and dry ammonium sulfate particles” by Tengyu Liu et al.**

Anonymous Referee #2

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In this manuscript, the authors conducted flow reactor photooxidation experiments of toluene, and examined the SOA formation in the presence of initially wet or dry ammonium sulfate seeds. The approach followed that of Faust et al. (2017) to eliminate the effect of water on the gas-phase oxidation mechanisms, and allows experimenters to focus on the effect of aqueous vs dry seeds on gas-particle partitioning of organics. High resolution aerosol mass spectrometry was used to probe bulk composition, and various mechanisms were proposed to explain the changes in oxidation state, m/z fragment signal fractions and overall mass yields.

The results from this work are qualitatively consistent with those from Faust et al.

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There are some questions regarding the oxidation mechanisms that lead to observed changes. My main criticism is that this work report mostly observational results, and lack any detailed mechanistic insights. The results are interesting, and can be explored more in order to provide useful information for both understanding the system and modeling the oxidation. I therefore suggest a few areas to look into, and the manuscript can be strengthened if the following questions are considered.

Major comments:

Oxidation mechanism: The major weakness in the paper is that it largely relies on bulk observation to probe mechanisms. While AMS is useful in obtaining bulk OA information and functional groups, the trends shown here are largely consistent with other aerosol aging observations in the lab or in the field. I am not sure if there are any novel insights in changes of m/z 43 and m/z 44, or the slope of the Van Krevelen diagram. It seems that the wet seed shows slightly different trends, but overall quite insignificant. The authors offer a few potential explanations (e.g. more OH aging, different gas-particle partitioning), but fail to go any deeper. If the explanation is more OH aging, then what is the equivalent change in OH exposure due to a wet seed (e.g. an OH exposure of 1 day at 65% RH is equivalent to an OH exposure of X days at 5%RH). Or, asking the question and framing the results in a different way: What is the increase in OH concentration in the aqueous phase that is required to explain the difference? Is this increase reasonable given the literature on aqueous OH production?

If the enhanced partitioning is due to availability of ALW, one can potentially explain the difference using Henry's law constants. What would the Henry's Law constants of the oxidation products need to be in order to show the difference in SOA yields between wet and dry seeds?

The approach used to calculate ALW separately for AS and toluene assume that they are linearly additive. In a metastable solution of ammonium sulfate, the ionic strength would be very high, and can affect the water solubility of the organics. Would it be

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valid to assume then the water uptake that cannot be explained by literature kappa of toluene SOA is associated with AS?

Experimental uncertainties: I am not sure if the experimental uncertainty in yields include only that from quantification of aerosol. The quantification of toluene reacted would play an important role as well, especially since the reported yields (with only uncertainty of SOA) have almost negligible uncertainty. In this work, toluene is not quantified, but the amount reacted is based on estimation of OH exposure. Other work in the literature quantifying yields measure the hydrocarbon precursor directly (using either PTRMS or GC methods). Offline quantification of OH exposure using SO₂ and assuming light conditions are constant can be problematic. There needs to be a systematic investigation of the uncertainties, particularly that associated with quantifying hydrocarbon decay.

Minor comments:

Abstract: Should be less focused on specific details of the experiments. I suggest taking some of the numbers out (unless it is a really important number that, for example, a modeler can use or another experimentalist can directly compare). Rather, there may be broader implications other than these results warrant further study. What are the detailed mechanistic insights? What further developments are needed to better understand water uptake? Just a few sentences would suffice.

Line 36: m/z 29, 43, 44 are specific to the aerosol mass spectrometer (AMS).

Line 47-48: these references might not quite reflect the current state of knowledge. For example, Tsigaridis et al. (ACP, 2014) did a model intercomparison and found that the secondary nature of OA can be reproduced, but not the overall amount. Shrivastava et al (ACP, 2011) shows that the total SOA amount can be reproduced, but require some model tuning. Overall, there may be too many studies to cite for a simple argument here, but the de Gouw et al. and Volkamer et al. studies are quite out of date at this point.

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Line 60: I would also add that understanding water uptake of SOA is important for estimating its loss by wet deposition, which is highly unknown at this point.

Line 97: is the silica gel diffusion dryer manufactured by TSI? If so, consider including the model number. Is the 30% outlet RH experimentally verified? I would imagine the outlet RH would be a function of the inlet RH

Line 103: Is it correct that the ALW is estimated using the method described later? If so, please mention.

Lines 140-146: Based on the OH exposure calculated, what is the amount of toluene consumed?

Line 166-167: is this filtered air flow with or without toluene and/or oxidation products?

Line 177: Just to make sure that sulfate is indeed coated with SOA, it would be great to show size distributions: Either a unimodal SMPS number size distribution showing no nucleation, or the PTOF on the AMS showing that organics and sulfate are in the same mode.

Line 187: Is it really evaporation of the organics? Would 8% mass loss due to evaporation be enough to show up in shifts in particle mode or median diameter (it would be around a ~2% change in diameter)?

Line 252: I suggest keeping all OH exposure numbers to 10^{11} molec cm⁻³ s. For example, I recommend changing 4.66×10^{10} to 0.47×10^{11} .

Line 290 – 292: The authors should be cautious about observations of oligomers on the AMS. The relatively low signal above m/z 80 does not mean there is little to no oligomerization. The AMS vaporizer at 600 C causes extensive thermal decomposition.

Line 298-303: Would a plot $f(28+44)$ vs $f(29+43)$ look different from f_{44} vs f_{43} ? The conversion of alcohols and aldehydes to acids described in the previous paragraph is fundamentally driving the trend of f_{44} and f_{43} . So these two paragraphs are both

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conveying a similar observation, which is expected given the extensive literature on AMS description of aerosol aging. So I suggest condensing the discussion.

Line 314-315, and Fig. S4: The differences seem very minute to me and may not be statistically significant. The y-scale is misleading, and should start at zero.

Line 314-315: If the trend is due to enhanced partitioning of water soluble organics to ALW, wouldn't the

Line 327: It looks like the subscript "C" in OSC is not capitalized, where it has been capitalized in other instances in the manuscript.

References: Tsigaridis, K., Daskalakis, N., Kanakidou, M., Adams, P. J., Artaxo, P., Bahadur, R., Balkanski, Y., Bauer, S. E., Bellouin, N., Benedetti, A., Bergman, T., Berntsen, T. K., Beukes, J. P., Bian, H., Carslaw, K. S., Chin, M., Curci, G., Diehl, T., Easter, R. C., Ghan, S. J., Gong, S. L., Hodzic, A., Hoyle, C. R., Iversen, T., Jathar, S., Jimenez, J. L., Kaiser, J. W., Kirkevåg, A., Koch, D., Kokkola, H., Lee, Y. H., Lin, G., Liu, X., Luo, G., Ma, X., Mann, G. W., Mihalopoulos, N., Morcrette, J.-J., Müller, J.-F., Myhre, G., Myriokefalitakis, S., Ng, N. L., O'Donnell, D., Penner, J. E., Pozzoli, L., Pringle, K. J., Russell, L. M., Schulz, M., Sciare, J., Seland, Ø., Shindell, D. T., Sillman, S., Skeie, R. B., Spracklen, D., Stavrou, T., Steenrod, S. D., Takemura, T., Tiitta, P., Tilmes, S., Tost, H., van Noije, T., van Zyl, P. G., von Salzen, K., Yu, F., Wang, Z., Wang, Z., Zaveri, R. A., Zhang, H., Zhang, K., Zhang, Q., and Zhang, X.: The AeroCom evaluation and intercomparison of organic aerosol in global models, *Atmos. Chem. Phys.*, 14, 10845-10895, <https://doi.org/10.5194/acp-14-10845-2014>, 2014.

Shrivastava, M., Fast, J., Easter, R., Gustafson Jr., W. I., Zaveri, R. A., Jimenez, J. L., Saide, P., and Hodzic, A.: Modeling organic aerosols in a megacity: comparison of simple and complex representations of the volatility basis set approach, *Atmos. Chem. Phys.*, 11, 6639-6662, <https://doi.org/10.5194/acp-11-6639-2011>, 2011.

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